PATENT SPECIFICATION

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COMPLETE SPECIFICATION.

Improvements in or relating to the Production of Glass-to-Metal Seals.

We, JOSEPH WOOLMAN, a British Subject, of 7, Chorley Drive, Sheffield, 10, Yorkshire, CHARLES SYKES, a British Subject, of 26, Crabtree Lane, Sheffield, 5, Yorkshire, and CHARLES STOKES, a British Subject, of 119, Dobcroft Road, Sheffield, 7, Yorkshire, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

Many alloys have been proposed and some are well known for making glass-to-metal seals. In general these alloys have been so selected as to composition that the thermal expansion characteristics of the alloy will match, or conform appropriately to, the corresponding characteristics of the glass. For many practical applications, it has been considered desirable that the alloy should have a slightly higher coefficient of thermal expansion than that of the glass to which it is to be sealed, so that when cold the glass will be in a controlled state of slight compressive stress. If, however, this difference is too great, cracking or stripping of the glass may occur.

The present invention is particularly (but not exclusively) concerned with alloys suitable for sealing to relatively soft glasses having coefficients of thermal expansion in the region of ·0000080 to ·000010 per degree centigrade over the range 20° to 500°C. Such glasses are common glass as used, for example, in the manufacture of plate glass having a coefficient of expansion of the order ·00000895 per degree centigrade, or another with an expansion coefficient of ·00000930 per degree centigrade, or a special high expansion glass with an expansion coefficient of ·00000972.

For the purpose of sealing to glasses of the above kind, it has hitherto been a general practice to employ chromium irons containing 16 to 30 per cent. of chromium. A drawback to the use of such alloys with a chromium content in the higher part (say 26-30%) of the range, is the difficulty of producing the alloys in suitable forms for subsequent use, since they have poor hot and cold working properties, in particular, they are difficult to spin or deep press. Efforts have been made to overcome these difficulties by various alloy additions, but these are only partially successful. In consequence, attention has been given to the alloys within the lower part of the chromium range, say 16 to 22% chromium, which are much easier to work. These, however, have a slightly higher coefficient of expansion than the 26 to 30% alloys and can only be used with reasonable success for sealing to special glasses having high coefficients of expansion. They also tend to suffer from transformation changes which have a deleterious effect on the sealing characteristics. One way of dealing with these transformation changes is to add stabilizing elements such as titanium, niobium, tantalum, aluminium, molybdenum, vanadium and tungsten, which suppress the transformation changes, or by using an alloy with a very low carbon content. These modifications to the plain chromium iron alloys, however, do not materially affect the normal thermal expansion rate and unless glasses with a suitable rate of expansion are selected trouble still arises by cracking or stripping of the glass.

Broadly stated the present invention comprises a method of making glass-to-metal seals which is characterised by the features that the metal is an alloy containing cobalt in a proportion of 0·1 to 10%, the metal is heated under oxidising conditions to a temperature at which oxidation of the cobalt will occur, the cobalt oxide is absorbed by the glass, so that the glass remains plastic at temperatures below its normal softening point, and the metal and glass are united under conditions which will ensure such absorption. As a result, despite appreciable difference in the rate of thermal expansion

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between the metal and the glass, excessive stresses cannot be built up, and substantially adhesive seals are obtainable with a wide variety of glasses. Indeed it has been found that satisfactory seals may be made even when the metal consists of an alloy of such composition that on heating or cooling transformation changes take place.

In the preferred method of carrying out the invention the metal of the seal is a chromium iron alloy containing 10 to 30% chromium. The preferred cobalt range is 1·0 to 3·0%. When making a seal the cobalt in the steel oxidizes to form cobalt oxide which is absorbed by the hot plastic glass in its vicinity and this modified glass is plastic at much lower temperatures than glass without cobalt oxide addition. As explained above, it is for this reason that successful seals without cracking or stripping are made possible by this invention. It has been found that the addition of cobalt is successful with alloys containing as low as 16 to 17% chromium, remainder substantially iron, even though when cold the alloy contains appreciable amounts of retained austenite (namely, 30%). Iron alloys, either of 17% chromium or 20% chromium or thereabouts, with the cobalt additions, are relatively easy to cold-work and to produce as spinnings and these alloys are, therefore, particularly advantageous in the manufacture of spun cones for cathode-ray tubes used in the Television Industry, and similar applications. It should be emphasised that the addition of cobalt does not materially alter the coefficient of expansion of the alloy.

We are aware of various prior proposals relating to alloys containing cobalt for glass-to-metal seals. There are for example the well known nickel-cobalt alloys of the "Kovar" (which is a Registered Trade Mark) or "Fernico" types, where cobalt is added in order to adjust the coefficient of expansion to the desired value. These alloys are expensive. They are only suitable for glass of the boro-silicate type and are not suitable for relatively soft glasses. A further proposal (see Specification No. 417751) relates to an alloy containing 70-85% tungsten and 15-20% nickel or the same proportion of nickel and cobalt, with a maximum of 5% cobalt; this again is an alloy chosen purely for its thermal expansion characteristics. A further proposal (see Specification No. 392421) concerns an alloy containing 30-50% nickel the remainder substantially iron, with a trace of cobalt said to be added as a fluxing material. Plain nickel and iron alloys are notoriously difficult to seal to glass and the cobalt in this case does improve the adhesion of the two materials. Again these alloys are selected as to composition in order to conform appropriately to the thermal expansion characteristics of the particular glass which is used.

The following are typical analyses of alloys which, in the practice of this invention, have given satisfactory seals to both types of plate glass available in this country, namely having coefficients of expansion of ·00000895 and ·0000093 per °C. respectively over the range 20° to 500°C.:—

C	Si.	Mn.	Cr.	Co.
%	%	%	%	%
0·07	0·42	0·67	21·14	2·20
0·09	0·30	0·70	17·0	1·80

In these alloys iron is the substantial remainder.

This invention includes, in glass-to-metal seals, alloys comprising carbon 0·2% maximum, chromium 10 to 30%, cobalt 0·1 to 10% and the remainder substantially all iron. The preferred range is carbon 0·1% maximum, chromium 16 to 22%, cobalt 1 to 3% and the remainder substantially all iron. Stabilizing elements such as titanium, niobium, tantalum, aluminium, molybdenum, vanadium and tungsten may also be present.

The invention also includes glass-to-metal seals (for electric filament lamps, cathode-ray tubes and the like) when made by methods involving the characteristic feature herein described.

What we claim is:—

1. A method of making a glass-to-metal seal involving the heating of the glass and metal to the softening point of the glass, characterised by the features that the metal is an alloy containing cobalt in a proportion of 0·1 to 10%, the metal is heated under oxidising conditions to a temperature at which oxidation of the cobalt will occur, cobalt oxide is absorbed by the glass, so that the glass remains plastic at temperatures below its normal softening point, and the metal and glass are united under conditions which will ensure such absorption.

2. A method according to Claim 1 in which the proportion of cobalt is 1·0 to 3·0%.

3. A method according to any one of the foregoing claims in which the metal of the seal is a chromium iron alloy containing 10 to 30% chromium together with the aforesaid cobalt.

4. A method according to any one of the foregoing claims applied to the sealing of chromium iron alloys to relatively soft glasses having coefficients of thermal expansion in the region of ·0000080 to ·000010 per degree centigrade over the range 20° to 500°C.

5. In a glass-to-metal seal made by a method according to any one of the preceding claims, chromium iron comprising carbon 0·2% maximum, chromium 10 to 30%, cobalt 0·1 to 10% and the remainder substantially all iron.

6. In a glass-to-metal seal made by a method according to any one of the preceding claims 1-4, chromium iron comprising carbon 0·1% maximum, chromium 16 to 22%, cobalt 1 to 3% and the remainder substantially all iron.

7. In a glass-to-metal seal according to Claim 5 or Claim 6, chromium iron which contains one or more of the following stabilizing elements:— titanium, niobium, tantalum, aluminium, molydbenum, vanadium and tungsten.

8. Glass-to-metal seals (e.g. for electric filament lamps, cathode-ray tubes and the like) when made by the method according to any one of the foregoing claims 1 to 4.

Dated this 28th day of February, 1951.

BOULT, WADE & TENNANT,
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Chartered Patent Agents.

PROVISIONAL SPECIFICATION

Improvements in or relating to the Production of Glass-to-Metal Seals

We, JOSEPH WOOLMAN, a British subject, of 7, Chorley Drive, Sheffield, 10, Yorkshire, CHARLES SYKES, a British subject, of 26, Crabtree Lane, Sheffield, 5, Yorkshire and CHARLES STOKES, a British subject, of 119, Dobcroft Road, Sheffield, 7, Yorkshire, do hereby declare this invention to be described in the following statement:—

Many alloys have been proposed and some are well known for making glass-to-metal seals. In general these alloys have been so selected as to composition that the thermal expansion characteristics of the alloy will match, or conform appropriately to, the corresponding characteristics of the glass. For many practical applications, it has been considered desirable that the alloy should have a slightly higher coefficient of thermal expansion than that of the glass to which it is to be sealed, so that when cold the glass will be in a controlled state of slight compressive stress. If, however, this difference is too great, cracking or stripping of the glass may occur.

The present invention is particularly (but not exclusively) concerned with alloys suitable for sealing to relatively soft glasses having coefficients of thermal expansion in the region of ·0000080 to ·000010 per degree centigrade over the range 20° to 500°C. Such glasses are common glass as used, ffor example, in the manufacture of plate glass having a coefficient of expansion of the order ·00000895 per degree centigrade, or another with an expansion coefficient of ·00000930 per degree centigrade, or a special high expansion glass with an expansion coefficient of ·00000972.

For the purpose of sealing to glasses of the above kind, it has hitherto been a general practice to employ chromium irons containing 16 to 30 per cent. of chromium. A drawback to the use of such alloys with a chromium content in the higher part (say 26-30%) of the range, is the difficulty of producing the alloys in suitable forms for subsequent use, since they have poor hot and cold working properties, in particular, they are difficult to spin or deep press. Efforts have been made to overcome these difficulties by various alloy additions, but these are only partially successful. In consequence, attention has been given to the alloys within the lower part of the chromium range, say 16 to 22% chromium, which are much easier to work. These, however, have a slightly higher coefficient of expansion than the 26 to 30% alloys and can only be used with reasonable success for sealing to special glasses having high coefficients of expansion. They also tend to suffer from transformation changes which have a deleterious effect on the sealing characteristics. One way of dealing with these transformation changes is to add stabilizing elements such as titanium, niobium, tantalum, aluminium, molybdenum, vanadium and tungsten, which suppress the transformation changes, or by using an alloy with a very low carbon content. These modifications to the plain chromium iron alloys, however, do not materially affect the normal thermal expansion rate and unless glasses with a suitable rate of expansion are selected trouble still arises by cracking or stripping of the glass.

According to the present invention the composition of the chromium iron is modified in such a way that the glass in contact with the alloy at the seal will be slightly modified by absorption of an element from the alloy and thereby be rendered more plastic at temperatures well below the normal softening temperature of the glass. As a result, despite appreciable difference in the rate of thermal expansion between the alloy and the glass, excessive stresses cannot be built up, and substantially stress-free seals are obtainable with good adhesion with a wide variety of glasses. Indeed, it has been found, that satisfactory seals may be made even when the alloy is such that on heating or cooling transformation changes take place.

The preferred method of carrying out the invention comprises the addition to the chromium iron alloy of 0·1 to 10% of cobalt, the preferred cobalt range being 1·0 to 3·0%. When making a seal the cobalt in the steel oxidises to form cobalt oxide which

is absorbed by the hot plastic glass in its vicinity and this modified glass is plastic at much lower temperatures than glass without cobalt oxide addition. As explained above, it is for this reason that successful seals without cracking or stripping are made possible by this invention. It has been found that the addition of cobalt is successful with alloys containing as low as 16 to 17% chromium, remainder substantially iron, even though when cold the alloy contains appreciable amounts of retained austenite (namely, 30%). Iron alloys, either of 17% chromium or 20% chromium or thereabouts, whether with or without the cobalt additions, are relatively easy to cold-work and to produce as spinnings and these alloys are, therefore, particularly advantageous in the manufacture of spun cones for cathode-ray tubes used in the Television Industry, and similar applications. It should be emphasised that the addition of cobalt does not materially alter the coefficient of expansion of the alloy.

We are aware of various prior proposals relating to alloys containing cobalt for glass-to-metal seals. There are for example well known nickel-cobalt alloys of the "Kovar" (which is a Registered Trade Mark) or "Fernico" types, where cobalt is added in order to adjust the coefficient of expansion to the desired value. These alloys are expensive and are only suitable for glass of the boro-silicate type. A further proposal (see Specification No. 417751) relates to an alloy containing 70-85% tungsten and 15-20% nickel or the same proportion of nickel and cobalt, with a maximum of 5% cobalt; this again is an alloy chosen purely for its thermal expansion characteristics. A further proposal (see Specification No. 392421) concerns an alloy containing 30-50% nickel, the remainder substantially iron, with a trace of cobalt said to be added as a fluxing material. Plain nickel and iron alloys are notoriously difficult to seal to glass and the cobalt in this case does improve the adhesion of the two materials. Again these alloys are selected as to composition in order to conform appropriately to the thermal expansion characteristics of the particular glass which is used.

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0·09	0·30	0·70	17·0	nil	1·80

This invention includes, for the making of glass-to-metal seals, alloys comprising carbon 0·2% maximum, chromium 10 to 30%, cobalt 0·1 to 10% and the remainder substantially all iron. The preferred range is carbon 0·1% maximum, chromium 16-22% cobalt 1 to 3% and the remainder substantially all iron. Stabilizing elements such as titanium, niobium, tantalum, aluminium, molybdenum, vanadium and tungsten may also be present.

The invention also includes glass-to-metal seals for electric filament lamps, cathode-ray tubes and other articles comprising a glass-to-metal seal whereof the metal is a cobalt-containing chromium iron as defined above.

In the foregoing description the invention has been illustrated in application to seals between glass and chromium-iron alloys. With other alloys the same difficulty may be experienced, from one cause or another, in matching the coefficient of expansion of the alloy with that of the glass to which it is to be sealed.

In such cases the difficulty may be solved by the addition of cobalt to the alloy so that when making the seal the cobalt will oxidise to form cobalt oxide which will be absorbed by the hot plastic glass in the vicinity of the seal. It is to be understood therefore that the present invention extends to the addition of cobalt, for the purpose described, to alloys other than those of chromium-iron.

Dated this 22nd day of August, 1950.

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Chartered Patent Agents.

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